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(Australian Petty Patent)

(54) Title  
ION EXCHANGING POLYMER

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(56) Prior Art Documents  
56311/86 B01J 43/00 B01D 35/06

(57) Claim

1. The use of a suitably modified polyurethane foam as the continuous phase and containing suitable ion exchange materials as the dispersed phase to produce an electrochemical ion exchange cell capable of recovering anions and cations from aqueous solution, then by reversing the polarity of the electrodes within the cell the ions so collected by the electrochemical cell may be eluted for disposal or recovery of these ions.

AUSTRALIA  
Patents Act 1990

629790

P/00/002 28.5.91  
Section 25

## PATENT REQUEST: PETTY PATENT

I / We, being the person(s) identified below as the Applicant, request the grant of a patent to the person identified below as the Nominated Person, for an invention described in the accompanying Petty complete specification.  
Full application details follow.

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[54] Invention Title AN ELECTROCHEMICAL PROCESS EMPLOYING A MODIFIED POLYMERIC FOAM TO ENHANCE THE RECOVERABILITY OF METAL IONS FROM SOLUTION

[72] Name(s) of actual inventor(s) WILLIAM HAROLD JAY

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Attorney Code

### ASSOCIATED PROVISIONAL APPLICATION(S) DETAILS

[60] Application Number(s) and Date(s)

### BASIC CONVENTION APPLICATION(S) DETAILS

[31] Application Number	[33] Country	Country Code	[32] Date of Application

### DIVISIONAL APPLICATION DETAILS

[62] Original application number

### TICK IF APPLICABLE

☒ I am an eligible person described in Sections 33 - 36 of the Act.

Drawing number recommended to accompany the abstract FIG 1.

William Jay  
(Signature)

27 July 1992  
(Date)

AUSTRALIA

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## NOTICE OF ENTITLEMENT

(To be filed before acceptance)

I/We, WILLIAM HAROLD JAY

of 64 TURANA ST, DONCASTER ACN/ARBN

being the applicant in respect of Application No. 18629/92, state the following:-

**Part 1 - Must be completed FOR ALL APPLICATIONS.**

The person(s) nominated for the grant of the patent:

\*is / \*are the actual inventor(s)

or

\*has entitlement from the actual inventor(s)

(eg by assignment, by mesne assignment, as legal representative of .... etc)

**\* Part 2 - Must be completed IF THE APPLICATION IS ASSOCIATED with one or more PROVISIONAL APPLICATIONS.**

The person (s) nominated for the grant of the patent:

\*is / \*are the applicant(s) of the provisional application(s) listed on the patent request form

or

has entitlement to make a request under Section 113 in relation to the provisional application(s) listed on the patent request form

(eg by assignment, by agreement, etc)

William Jay  
(Signature)

27 July 1992  
(Date)

(If the applicant is a Company or other legal entity, also indicate the name and standing of the authorized signatory.)

\* Omit/Delete if not appropriate

**Note:** Use form P/00/008b where details for PCT, convention priority, microorganism deposit, additional or divisional application, are required.

AUSTRALIA

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PETTY PATENT SPECIFICATION.

Application Number:

Lodged:

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64 Turana Street, Doncaster, in the  
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Petty Patent Specification for the invention entitled:

"AN ELECTROCHEMICAL PROCESS EMPLOYING A MODIFIED POLYMERIC  
FOAM TO ENHANCE THE RECOVERABILITY OF METAL VALUES FROM  
SOLUTION."

The following statement is a full description of this invention  
including the best method of performing it known to us:-

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The present invention relates to the production of an open cellular polymeric material containing as a dispersed phase an ion exchange material. The polymer may be rendered electrically conducting if required, by incorporation into its structure an electrically conducting polymer or additive. Ion exchange is controlled by application of an electrode potential between the open-cellular polymeric material and the counter electrode. By suitably charging the electrode the ion exchange resin present in the polymer will either recover metal ions from solution, or elute the metal ions for subsequent recovery.

The present invention may be used for applications such as recovery of precious metals from solution; the removal of toxic or heavy metals from wastewater streams; removal of corrosive anions, water deionisation, etc. The invention is not limited to the above applications, but can be also applied to other aqueous streams for removal of other cations, anions, radionuclides etc.

In traditional technology recovery or removal of metal ions from aqueous solution is accomplished by cementation processes, precipitation following pH control, activated carbon sorption, ion exchange, solvent extraction or other known technology.

Electrochemical ion exchange (EIX) has been proposed by Bridger, Jones & Neville, Electrochemical Ion Exchange, J. Chem. Tech. Biotechnol. (1991), 50, 469-481 and they favourably compared the performance of their cell with electrodialysis and also electrodialysis combined with conventional exchange for the removal of cations and anions from aqueous solution.

The Cell proposed by Bridger, et al. was manufactured by grinding commercial ion exchange materials to a fine powder of mean particle size approximately 0.1 mm then mixing this with a synthetic rubber binder dissolved in a solvent, pouring the binder solution into a mould containing platinised titanium mesh electrodes and allowing the solvent to evaporate.

This process involves a suitable polyurethane foam containing an ion exchange resin dispersed throughout its matrix such as disclosed by Braun, Bekeffy, Haklits, Kadar & Majoros in Anal. Chim. Acta (1973), 64, 45-54. The polyurethane foam containing the ion exchange resin may be made suitably electrically conductive. This modified polymeric foam forms the cellular portion of the electrochemical cell.

This patent extends the design and performance of Bridger's electrode by significantly increasing the available surface area of the electrochemical cell by allowing the ion exchange material which has been dispersed throughout the polyurethane polymer to rapidly contact the aqueous phase improving the kinetics of the removal of metal ions from solution. The cross section of a typical EIX electrode is shown in Figure 1.

The polyurethane foam may be reticulated (remove cell "windows" remaining within the foam after curing) by known technology such as explosion technology in which a hydrogen-oxygen flame front rapidly spreads through the open-cell polyurethane foam under controlled conditions.

The aim of the present invention is to provide an improved process for the removal of anions and/or cations from aqueous solution in which the exchange process is controlled electrochemically and therefore the use of chemicals to regenerate the ion exchange resin is eliminated. Furthermore, it is possible to elute the recovered metal ion in a single bed-volume thus achieving a large volume reduction of eluent.

The electrically conducting open cell polymer containing the ion exchange beads provides a large surface area to enhance the rate of uptake of the ion from the aqueous solution. This substantial increase in surface area allows the overall size of the process equipment to be decreased thereby reducing the cost of the recovery equipment. There is also an increase in the overall removal rate of ions from solution for the same volume as a greater volume of solution is in contact with the polymer at any one time. The ability to use a range of inorganic and/or organic ion exchange materials makes it possible to achieve a degree of selectivity.

Polyurethane resins are employed to produce the continuous phase of the modified polymeric foam and either acid based cation exchangers and/or basic anion exchangers form the discontinuous phase. Such ion exchange resins may be based on organic resins (for instance polystyrene-divinylbenzene resins containing carboxylate groups), inorganic ion exchangers (such as zirconium phosphate), secondary, tertiary or quaternary ammonium moieties, etc.

Electrical conductivity throughout the polymer can be achieved by incorporation into the polyurethane phase an electrical conductor such as carbon. Metals such as gold, platinum group elements, etc. can, if required, be deposited on to the surface of the carbon. Alternatively, an electrically conducting polymer such as polyaniline, polyacetylene, polypyridyl, etc., can be incorporated into the polyurethane resin. This process is not limited to these particular mechanisms of providing electrical conductivity.

Application of an electrical potential across the cell encourages the migration of ions within the cell; anions migrating to the anode, and cations to the cathode. This movement of ions enhances both the sorption and elution processes involved in removal of the ions from solution. For instance, in removal of metal ions from solution the electrode is made to be the cathode during the sorption operation as shown in Figure 2, and the anode as shown in Figure 3 during the elution step.

During the sorption reaction the active group, typically a carboxylic acid group is deprotonated to give an overall negative charge:



where R represents the backbone of the ion exchange resin.

In order to maintain a charge balance, a cation,  $\text{M}^+$  is absorbed



Elution is accomplished by the reprotonation of the active group:



The corresponding anion exchange reactions could involve protonation and deprotonation of secondary or tertiary ammonium groups on the resin such as,

Activation:



Sorption:



Elution:



When the ion-exchange electrode is absorbing, the hydroxide ions produced on the central electrode deprotonate the carboxylic acid groups on the exchanger. For current to flow, cations are transported through the electrode matrix to occupy vacant sites. Similarly, migration also occurs during anion exchange.

In an operating electrochemical cell, a counter electrode reaction occurs simultaneously and in the case of cation electrochemical ion exchange this involves the production of hydrogen ions thereby decreasing the pH of the external solution. These ions will be absorbed as an interfering ion slowly deactivating the electrochemically activated site by recombination.

The electrochemical ion exchange cell can be operated in either batch or continuous flow modes. It is possible by recycling the effluent from a continuous system to operate it in a batch mode.

BAD ORIGINAL

CLAIM.

1. The use of a suitably modified polyurethane foam as the continuous phase and containing suitable ion exchange materials as the dispersed phase to produce an electrochemical ion exchange cell capable of recovering anions and cations from aqueous solution, then by reversing the polarity of the electrodes within the cell the ions so collected by the electrochemical cell may be eluted for disposal or recovery of these ions.



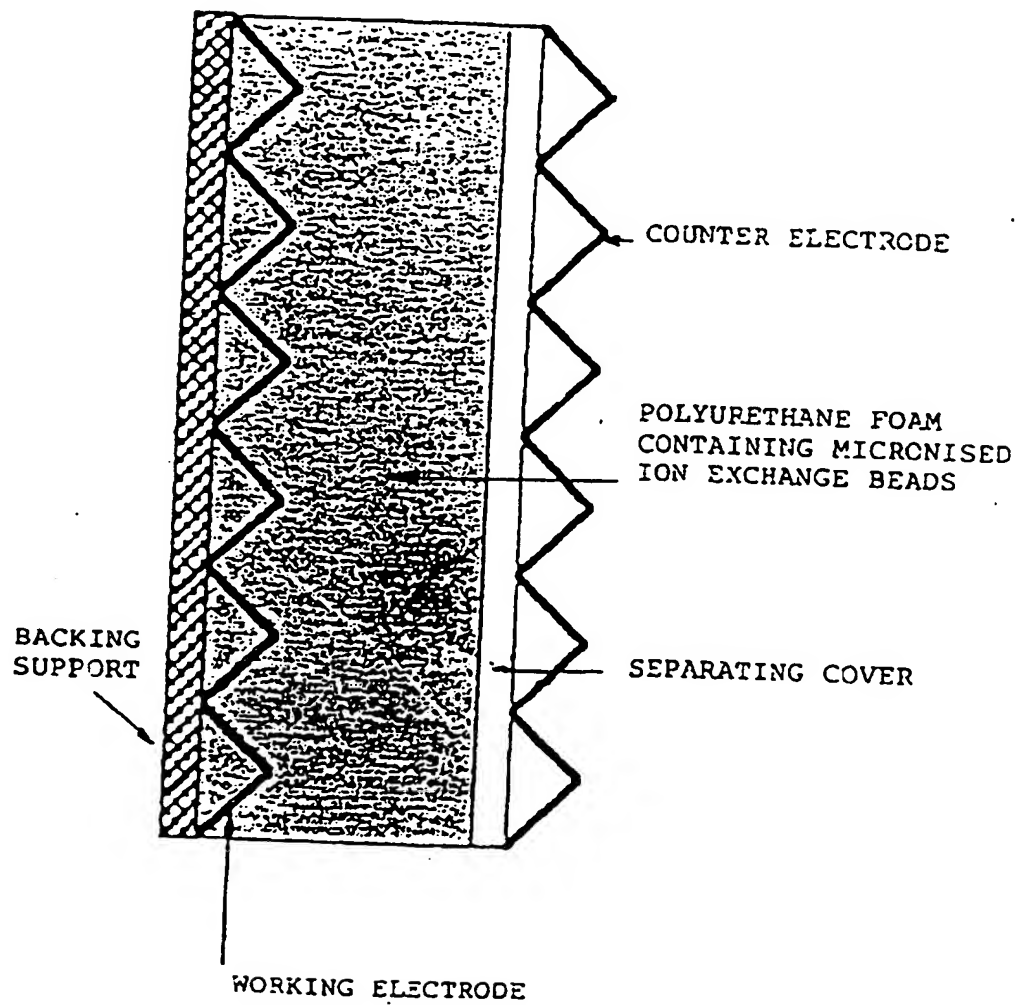


Fig. 1. CROSS SECTION OF A TYPICAL EIX ELECTRODE

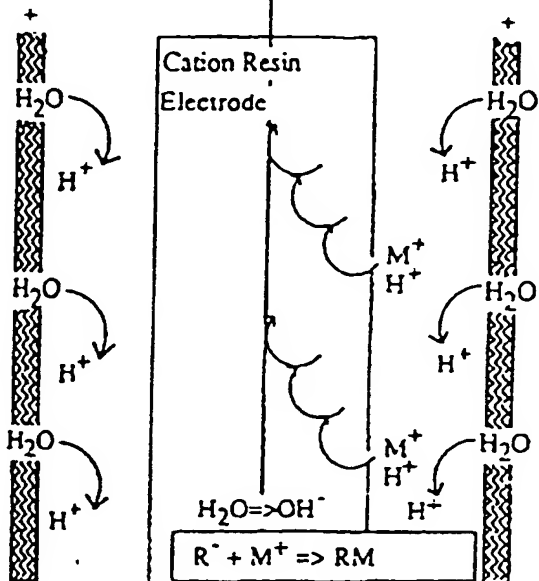


Fig. 2. ION MIGRATION DURING CATION SORPTION

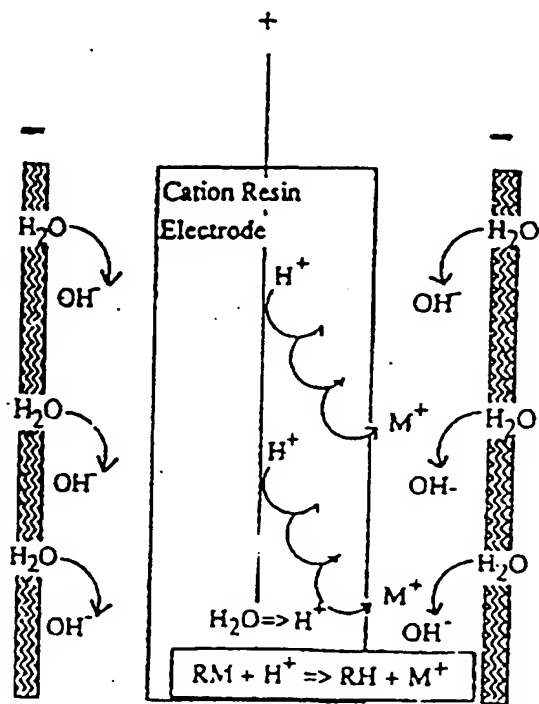


Fig. 3. ION MIGRATION DURING CATION ELUTION